

Implementing Safer Alternatives to Lithographic Cleanup Solvents to Protect the Health of Workers and the Environment

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The use of volatile organic compounds (VOCs) in lithographic printing cleanup is an environmental and occupational hazard. Regulations to reduce ambient ozone levels limited VOC emissions from lithographic cleanup operations and spurred the development of low-VOC alternatives. The purpose of this project was to promote the substitution of hazardous cleanup solvents with less toxic chemicals to protect the health of workers and the environment. A convenience sample of printers, employers, union, industry, and government representatives was constructed. Data regarding the lithographic printing work force and the use of cleanup solvents and alternatives were collected through: (1) work site walk-throughs, (2) a focus group, (3) key informant interviews, (4) a half-day workshop, and (5) demonstration projects. Overall, 66 individuals from 15 different print shops, 10 government agencies, the lithographic printing industry, and one printer's union participated in one or more aspects of the project. Printer inhalation exposure to hazardous cleanup solvents was prevalent and printers were not aware of safer alternatives. Employers should implement low-VOC, low-toxicity cleanup products in a timely manner to protect the health of printers and the environment. Use of low-VOC lithographic cleanup products does not mitigate the potential for printer dermal exposure and may carry safety and ergonomic implications. Lithographic cleanup solvent manufacturers should seek low-VOC ingredients that do not pose a dermal exposure hazard. Linking environmental and occupational health prevented the development of substitutes that would have introduced worker hazards and provided an opportunity to circumvent some of the inadequacies of the current occupational health regulatory apparatus. Governmental organizations should establish and maintain institutional interdisciplinary mechanisms to support these linkages.

Keywords alternatives, cleanup solvents, lithographic printers, printers, methyl esters

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INTRODUCTION

Lithographic printers use organic solvents with acute and chronic toxicity to clean the ink-coated cylinders of the printing press, and adverse health impacts are associated with exposure to these solvents.^(1–7) The use of cleanup solvents in lithographic printing also releases volatile organic compounds (VOCs) into the air where they mix with oxides of nitrogen in the presence of sunlight to form ozone. Exposure to ozone results in significant health impacts ranging from decreased lung function and increased respiratory symptoms to serious morbidity and mortality.^(8–10)

Beginning in 1991, California's South Coast Air Quality Management District (SCAQMD) promulgated Rule 1171 to reduce VOC emissions from solvent cleaning operations as a key component of the agency's ozone reduction strategy.⁽¹¹⁾ Several years ago, SCAQMD established a future VOC content limit of 100 g/L for cleaners used for on-press lithographic blanket and roller cleaning. This future VOC limit spurred government-funded research and development of low-VOC substitutes (i.e., cleaning agents with ≤ 100 g/L VOC content) for lithographic printing cleanup. Implementation of low-VOC lithograph printing cleanup products developed by the Institute for Research and Technical Assistance (IRTA) has the potential to also protect worker health.^(12,13) The SCAQMD regulation became effective in January 2008, but at that time, the environmental and occupational health benefits of the regulation had not accrued to areas outside the agency's purview. With an estimated 5600 to 8300 lithographic printers in California and 44,500 to 54,000 in the United States, many workers would benefit from implementation of safer alternatives.

A project was undertaken to promote implementation of safer alternatives to toxic lithographic cleanup solvents to prevent chronic health damage to printers in the San Francisco Bay Area. The objectives of the project were to: (1) identify

lithographic printers potentially at risk for solvent-related health problems; (2) evaluate solvents used by the printers, including hazard controls and knowledge of the health hazards; (3) identify existing less toxic solvent alternatives; and (4) elucidate opportunities and barriers related to using safer solvent alternatives in lithographic printing facilities.

METHODS

Selection Criteria

A convenience sample of printers, employers, union, industry, and government representatives was constructed as follows: (1) the executive director of IRTA (KW) invited participation from print shop employers she had worked with in the SCAQMD alternative cleanup solvent technology assessment; (2) based on the experience of the researchers, a short list of individuals with relevant knowledge of the lithographic printing industry (i.e., key informants) was developed, and in turn, these initial contacts were asked to suggest other interviewees; (3) a union representative was asked to recruit printers for a focus group; (4) the collaboration of two local government Green Business Coordinators was sought; and (5) an invitation to a workshop was mailed to 173 lithographic print shops listed by the Bay Area Air Quality Management District, the City and County of San Francisco, and Alameda County.

Data Collection

Data regarding the lithographic printing work force and the use of cleanup solvents and alternatives were collected between August 2006 and March 2007 by a variety of methods:

Work Site Walk-Throughs of Lithographic Print Shops

An industrial hygienist walked through the printing facility and directly observed the type and quantity of cleanup solvents in use and the presence and use of exposure control measures. At three facilities, the California Department of Public Health Hazard Evaluation System and Information Service's (HESIS) toxicologist also observed the work process. Using a detailed industrial hygiene checklist, employer representatives and printers were queried about the work process, job tasks, cleanup solvent use, exposure control measures, and the employer's health and safety program.

Focus Group

A focus group of lithographic printers was organized by a union representative and held at the union's office. Over a period of 4 hours, the HESIS toxicologist discussed the health effects of the cleanup solvents currently in use at the printers' shops, printers were asked to respond to 15 questions related to their use of cleanup solvents, and an industrial hygienist took written notes of their responses.

Key Informant Interview

A loosely structured conversation by phone or in person was conducted to elicit interviewees' knowledge of the issue of

cleanup solvent use in lithographic printing and opportunities and obstacles to implementing safer alternatives.

Workshop

A half-day interactive workshop was conducted on safer alternatives to printing cleanup solvents in collaboration with local, state, and federal government agencies and a union. An industrial hygienist took written notes of the discussion sections of the workshop.

Participation in the project was voluntary. The study protocols were reviewed by the University of California Berkeley Committee for Protection of Human Subjects, which found them to be exempted provided the information obtained would be recorded in such a manner that subjects could not be identified directly or through identifiers linked to the subjects, or, that the information obtained was publicly available.

All data on efficacy (i.e., whether a cleaning agent effectively cleaned the ink from the rollers or the blankets in a reasonable period of time to the satisfaction of print shop personnel) and environmental and occupational health impacts of safer alternative cleanup products were compiled from the SCAQMD technology assessment previously conducted by the IRTA.^(12,13)

Data Analysis

For each cleanup solvent product identified, the material safety data sheet (MSDS) was reviewed by the HESIS toxicologist to determine the identity (Chemical Abstract Service [CAS] number) and the percentage by weight of each of the product's chemical constituents. All workplace, focus group, key informant, and workshop information was compiled and summarized using descriptive statistics.

Evaluation Criteria

Worker exposure to cleanup solvents was qualitatively assessed by the industrial hygienist by considering the following criteria: (1) the potential for one or more routes of worker exposure; (2) the presence, use, and efficacy of measures to limit worker exposure; and (3) the presence of worker training and hazard communication about cleanup solvent exposure. The potential occupational health impacts of cleanup solvent exposure were assessed by the toxicologist by comparing each of the product's constituents as listed on its MSDS with its acute and chronic health effects as described in the scientific literature. The environmental health impact of the products evaluated was assessed by comparing the VOC content with the 100 g/L criteria established by SCAQMD's Rule 1171. In addition to toxicity and VOC content, alternative cleanup solvents were previously evaluated as part of the SCAQMD technology assessment by a chemist and one or more printers based on performance, press compatibility, and cost.^(12,13)

RESULTS

Data Collection

Overall, 66 individuals from 15 different print shops, 10 government agencies, the lithographic printing industry, and one printer's union participated in one or more aspects of the project. Data were gathered from: five on-site workplace walk-throughs involving 13 printers and/or employer representatives; one focus group with five printers from three shops ranging in size from six to 35 employees and one union representative; and 12 key informant interviews with representatives of government agencies ($N = 9$), a union, the printing industry, and a printer; and a total of 48 workshop participants including 25 individuals representing government agencies (1 federal, 4 state, and 5 local agencies), 16 printers from 10 shops, five environmental compliance consultants, managers, or human resources personnel, a union representative, and a printing industry representative.

Workplace Observations

The five print shops observed ranged in size from 6 to 157 printers and had a variety of web and sheet-fed presses (Table I). Two print shops had been previous participants in the SCAQMD technology assessment; two were recruited after they participated in the focus group, and one was invited to participate by the San Francisco Public Health Department Green Business Coordinator. Printers at all of the shops cleaned the presses' blankets and rollers by hand either exclusively or as a supplement to automated wash systems. To clean the blankets by hand, printers applied the solvent to a wipe cloth and wiped it across the blanket to remove the ink. Printers hand cleaned the ink roller train by holding a squeeze bottle above the rollers and dispensing the cleaner in a stream across the length of the top roller, and then applying pressure to the rollers with a squeegee or cloth. An ink tray lined with a wipe cloth was placed at the bottom of the roller train to catch the solvent/ink combination after it passed through the train. Used solvent-soaked cloths were stored in containers with lids and sent to a commercial laundry for washing.

The three print shops that provided quantitative data used from 0.7 to 36 gallons of cleanup solvents daily. Printers cleaned the presses on an intermittent basis throughout the day. Each cleanup generally took a few minutes. At one shop, a more thorough press cleanup reportedly conducted on a weekly basis was observed to last over an hour. Three shops estimated a printer's direct exposure to cleanup solvents totaled from one-half to two hours a day. Nitrile gloves were available for cleaning the press in all five shops; hand cleaning without the use of gloves was observed at one shop. None of the print shops routinely used local exhaust ventilation or respiratory or eye protection while handling cleanup solvents. The two smaller shops (< 35 employees) also had no mechanical dilution ventilation systems.

Health Impacts of Chemicals in Cleanup Solvents

A total of 20 MSDSs for high-VOC cleanup products were obtained as follows: 7 were provided by four of six print shops participating in the workplace walkthrough and/or focus group, and 13 had been obtained by IRTA from print shops that participated in the SCAQMD technology assessment (Table II). The MSDSs for the 20 products included 31 hazardous ingredients, and the majority of products (15 of 20) contained more than 60% organic solvents (Table III). Thirteen cleanup products contained one or more chemicals with recognized chronic health impacts beyond general solvent toxicity, including cancer, blood abnormalities, asthmatic bronchitis, peripheral nerve damage, and reproductive/developmental effects, and 10 products contained chemicals with "skin notations" (Table II).

Health Impacts of Chemicals in Alternative Products

MSDSs for 14 alternative low-VOC cleanup products were previously identified and evaluated in the SCAQMD technology assessment (Table IV). The MSDSs for the 14 products included 20 hazardous ingredients (Table V). Of 14 alternative cleaners, 4 had no hazardous ingredients listed on the MSDSs, 4 were formulated from fatty acid esters and surfactants alone or in combination, and 6 from one or more organic solvents (Table IV).

Focus Group

All five printers shared a general recognition that use of cleanup solvents could impact their health and a concern about the damage that may have already accrued from their chronic exposures. Cancer and reproductive health hazards were specific concerns. None of the printers was aware of the existence of safer alternatives, and all reported receiving some training about chemical hazards.

Demonstration Project

Two print shops, one large and one small, had expressed interest in converting to safer alternatives and both were invited to participate in a demonstration project conducted by IRTA's executive director.

At the small shop, soy- and acetone-based alternative cleanup products were manually tested on two sheet-fed presses. Soy Gold 2500 followed by a plain water rinse was tested as a roller wash, and Rho-Solv 7248 was tested as a blanket wash. To prevent a fire hazard, manufacturers of automated blanket and roller wash systems recommend using materials with a flash point of 140°F or greater. Based on its flash point, the soy product was suitable for automated systems, but the acetone-based product was not. Both alternatives tested met the performance expectations of the printers. Two shopwide conversion scenarios were calculated based on the volume of blanket and roller cleanup solvents currently purchased and the fact that the soy but not the acetone product could be used in automated systems. The cost analysis assumed that converting to alternatives would require the same amount of product and labor as the cleanup solvents currently in use.

TABLE I. Cleanup Solvent Use at Five Lithographic Print Shops

Print Shop	Press Type(s)	No. Employees	Cleanup Solvent		Ventilation	Gloves	Respiratory Protection	Training and Hazard Communication
			Use (Gallons per Day)	Nature of Cleanup Solvent Use				
1	Sheet-fed	20 (7 press operators)	~ 0.7	Depending on the press, blanket and roller cleaning is done exclusively by hand or by a combination of automatic blanket and/or roller wash systems. Approximately 30–45 min/day/printer to clean press at the time of a job or color changes and/or the end of the day. All presses with automated systems are also routinely cleaned by hand. Blanket on press with automatic wash system is cleaned by hand nightly. The automatic blanket wash system itself is cleaned by hand once a week, a task that takes 1–2 hr.	No LEV or HVAC system	Nitrile gloves available; inconsistent use observed among workers	None	On employment and annually
2	Sheet-fed	6	NA	Hand cleaning exclusively, approximately 30 min/day/printer.	No LEV or HVAC system	Nitrile gloves observed in use	None	On employment and annually
3	Web	157 printers	10	Hand cleaning approximately 30–40 min/day/printer.	HVAC system; NA LEV	Nitrile gloves reported to be in use	None	NA
4	Sheet-fed and web	126 printers and 24 floor helpers	30–36	Hand cleaning to supplement automated blanket and roller wash systems. Blanket cleaned at least one time per shift by hand; may be two times or more often depending on job.	HVAC system and LEV	Nitrile gloves observed in use	Yes. For biannual deep cleaning of web press and for breakdown and repair	On employment and annually
5	Sheet-fed	NA	NA	Hand cleaning to supplement automated blanket and roller wash systems.	NA	Nitrile gloves observed in use	None observed	On employment and annually

Note: NA = information not available.

TABLE II. Hazardous Ingredients in Lithographic Cleanup Products by Product (N=20 products)

	Product and Manufacturer (MSDS Date)	Chemical	Concentration % (w/w)	CAS No.	Additional Health Effects^A
1	Super Clean BW (3/11/01) Super Chem Corp., Anaheim, CA	Ethylphenoxy polyethoxy-ethanol D-Limonene	Not given Not given	9036-19-5 5989-27-5	Skin irritation and allergic contact dermatitis ⁽¹⁴⁻¹⁶⁾
2	Pressroom Solutions Blanket & Roller Wash 5001-5 (3/9/00) Pressroom Solutions, Fort Worth, TX	Aromatic hydrocarbons 1,2,4-Trimethyl benzene	10-15 3-5	64742-95-6 95-63-6	
3	IC ALL PRO (11/18/01) IC Compound Company, Gardena, CA	Aliphatic hydrocarbons Mineral spirits	85-90 Not given	64742-88-7 64742-88-7	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Aromatic hydrocarbon distillates	Not given	6472-95-6	
4	LC-1700 Press Wash (8/03) Litho-Chem, Inc., Sante Fe Springs, CA	2-Propoxy ethanol 2-Propanone	Not given 1-10	2807-30-9 67-64-1	Blood abnormalities ⁽¹⁹⁾
		Aliphatic hydrocarbon	>60	6742-89-8	
5	AQ 1301 Roller Wash No. 1 (10/02) Litho-Chem, Inc., Sante Fe Springs, CA	Aliphatic hydrocarbon	30-60	8008-20-6	Blood abnormalities ⁽¹⁹⁾
		Aromatic hydrocarbon	10-30	64742-95-6	
6	AQ 1302 Roller Wash No.2 (10/98) Litho-Chem, Inc., Sante Fe Springs, CA	Glycol ether ^B Aliphatic hydrocarbon	1-10 70-80	111-76-2 8052-41-3	Blood abnormalities ⁽¹⁹⁾
		Aromatic hydrocarbon	15-25	64742-95-6	
7	PowerKlene VC Blanket and Roller Wash (6/10/97) Printers' Service Newark, NJ	Glycol ether ^B Aromatic petroleum distillate (C8-C12)	7-12 40-50	111-76-2 64742-95-6	Blood abnormalities ⁽¹⁹⁾
		Aliphatic petroleum distillate (C9-C11)	40-50	64742-46-9	
		Dipropylene glycol methyl ether ^B	1-10	34590-94-8	
		(+)-4-Isopropenyl-1- methylcyclohexene	1-10	5989-27-5	
		Sorbitan monoleate	1-10	1338-43-8	

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TABLE II. Hazardous Ingredients in Lithographic Cleanup Products by Product (N=20 products)(Continued)

8	Hydro Clean Water Activated Press Cleaner (8/1/98) Lee Chemical Co., Los Angeles, CA	Mineral spirits	Not given	64742-47-8	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Hydrotreated distillate, light	Not given	8052-41-3	
		Xylene	Not given	1330-20-7	
		1,3,5-Trimethyl benzene	Not given	108-67-8	
		1,2,4-Trimethyl benzene	Not given	95-63-6	
9	Low VOC 1.68 Blanket Wash (8/10/96) A.G. Layne Inc., Los Angeles, CA	Isopropylbenzene ^B	Not given	98-82-8	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Acetone	Not given	67-64-1	
		Solvent naptha, light aliphatic	Not given	64742-89-8	
		Xylene	Not given	1330-20-7	
		1,2,4-Trimethyl benzene	Not given	95-63-6	
10	Blanket Wash (2/20/03) Bay International Chemical Products, Addison, IL	Solvent naptha, light aromatic	Not given	64742-95-6	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Petroleum naptha	53	64742-47-8	
		Petroleum naptha	28	64742-95-6	
		1,2,4-Trimethyl benzene	11	95-63-6	
		Dipropylene glycol methyl ether ^B	3	34590-94-8	
11	Allied Hydrowash (8/22/96) Allied Photo Offset Supply Corp., Hollywood, FL	Xylene	1	1330-20-7	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Aromatic petroleum distillates	50	64742-95-6	
		Xylene	2-5	1330-20-7	
		Cumene ^B	1-4	98-82-8	
		1,2,4-Trimethyl benzene	24-29	95-63-6	
12	Anchor Envirowash 220 (3/14/03) Anchor Lithkemko, Orange Park, FL	Aliphatic petroleum distillates	46	64741-41-9	(Continued on next page)
		Aliphatic hydrocarbon	10-20	64742-88-7	
		Aromatic hydrocarbons	5-10	7069306-0	
		Fatty acid ester TSRN 06-0836 -331-5005	15-30	not clear, number provided yielded no results	
		Aliphatic hydrocarbon	50-70	64741-47-5	

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TABLE II. Hazardous Ingredients in Lithographic Cleanup Products by Product (N=20 products)(Continued)

13	Shell Mineral Spirits 146 HT (1/21/90) Shell Oil Co., Houston, TX	Mineral spirits	100	64742-88-7	
14	Wash A-230 (2/1/00) Varn Products, Addison, IL	Petroleum naphtha	90	64742-88-7	
		Petroleum naphtha	5	64742-95-6	
		1,2,4-Trimethyl benzene	2	95-63-6	Blood abnormalities/ asthmatic bronchitis ^(17,18)
15	Wash V-120 (2/1/00) Varn Products, Addison, IL	Petroleum naphtha	43	64742-88-7	
		Petroleum naphtha	32	64742-95-6	
		1,2,4-Trimethyl benzene	12	95-63-6	Blood abnormalities/ asthmatic bronchitis ^(17,18)
		Dipropylene glycol methyl ether ^B	6	34590-94-8	
		1,8(9)-p-Methadiene	2	5989-27-5	
		Xylenes	1	1330-20-7	
16	Type Wash (2/1/00) Varn Products, Addison, IL	Toluene ^B	54	108-88-3	Developmental effects ⁽²⁰⁾
		n-Hexane and mixed isomers ^B	21	110-54-3	Peripheral nerve damage ⁽⁷⁾
		Isopropanol	25	67-63-0	
17	V-1106 Rejuvenator Plus (10/23/98) Varn Products, Addison, IL	Petroleum naphtha	35	8032-32-4	
		Diacetone alcohol	5	123-42-2	
		Propylene glycol t-butyl ether	5	57018-52-7	Cancer ⁽²⁰⁾
		Toluene ^B	5	108-88-3	Developmental effects ⁽²⁰⁾
		Isopropanol	<5	67-63-0	
		Dichloromethane	44.95	75-09-2	Cancer ⁽²⁰⁾
18	Mr. Murphy's Maticlean (8/21/96) Base-Line, Inc., Auburn, WA	2-Butoxyethanol ^B	60+	111-76-2	Blood abnormalities ⁽¹⁹⁾
19	Metering Roller CL-NC (1/1/97) Anchor Lithkemko, Orange Park, FL	Lacolene (aliphatic hydrocarbon)	85-100	64742-89-8	
20	Color Wash Step-1 (2/1/00) Varn Products, Addison, IL	Petroleum naphtha	59	64742-47-8	
		Petroleum naphtha	10	64742-94-5	

Note: Hazardous ingredients as listed in Section II of product MSDS.

^AHealth effects in addition to general solvent toxicity, with the exception of Product #1, Super Clean BW, which does not contain chemicals with general solvent toxicity.

^BSkin notation, significant amounts of chemical can be absorbed through the skin and contribute to systemic toxicity.

The cost of converting was calculated to reduce current annual expenditures for cleanup products (\$3708) 3 to 8%, depending on the ratio of soy to acetone product used.

At the large shop, soy- and acetone-based alternative cleanup products were tested manually on one sheet-fed press. Two blanket washes were tested: (1) Rho-Solv 7248, and (2) a mixture of 50 percent Soy Gold 2500 and 50% water. The 50/50 mixture was evaluated because the press's automated system sprayed a blend of 50% solvent and 50% water. The workers who cleaned the blankets reported both blanket washes performed well. Rho-Solv 7248 and Soy Gold 2500 were also tested by the on-site ink manufacturer who found them

effective for his cleanup tasks. One roller wash was tested: Soy Gold 2500 followed by plain water rinse. The supervising pressman was dissatisfied with the quality of the print color subsequent to the roller cleaning test.

Opportunities and Barriers

Opportunities and barriers to implementing safer alternatives existed among all populations that influenced decisions regarding cleanup solvent use (i.e., printers, employers, governmental and nongovernmental organizations, printing press manufacturers, chemical companies, and vendors) and arose across all aspects of the production process, beginning with the

TABLE III. Hazardous Ingredients in Lithographic Cleanup Products by Chemical (N=31 chemicals)

	Hazardous Ingredients	Chemical Abstract Number (CAS #)	Number of Products with CAS #	Concentration % (w/w)
1	Aromatic hydrocarbons	64742-95-6	10	Not given to 50
2	1,2,4-Trimethyl benzene	95-63-6	7	Not given to 29
3	Aliphatic hydrocarbons	64742-88-7	6	Not given to 100
4	Xylene	1330-20-7	4	Not given to 5
5	2-Butoxyethanol (ethylene glycol monobutyl ether) ^A	111-76-2	3	1–60
6	Dipropylene glycol methyl ether ^A	34590-94-8	3	1–10
7	D-Limonene	5989-27-5	3	Not given to 10
8	Mineral spirits	64742-47-8	3	Not given to 59
9	Toluene ^A	108-88-3	2	5–54
10	Solvent naptha, light aliphatic	64742-89-8	2	Not given to 100
11	Isopropanol	67-63-0	2	< 5–25
12	Acetone	67-64-1	2	Not given to 10
13	Aliphatic hydrocarbon	8052-41-3	2	Not given to 80
14	Cumene ^A	98-82-8	2	Not given to 4
15	n-Hexane and mixed isomers ^A	110-54-3	1	21
16	Diacetone alcohol	123-42-2	1	5
17	Sorbitan monoleate	1338-43-8	1	1 to 10
18	2-Propoxy ethanol	2807-30-9	1	Not given
19	Propylene glycol t-butyl ether	57018-52-7	1	5
20	Aliphatic petroleum distillates	64741-41-9	1	46
21	Aliphatic hydrocarbon	64741-47-5	1	50–70
22	Aliphatic petro distillate (C9–C11)	64742-46-9	1	40–50
23	Petroleum naptha	64742-94-5	1	10
24	Aliphatic hydrocarbon	6742-89-8	1	> 60
25	Aromatic hydrocarbons	70693-06-0	1	5–10
26	Dichloromethane (methylene chloride)	75-09-2	1	45
27	Aliphatic hydrocarbon	8008-20-6	1	30–60
28	Petroleum naptha	8032-32-4	1	35
29	Ethylphenoxypolyethoxy-ethanol	9036-19-5	1	Not given
30	Fatty acid ester TSRN 06-0836-331-5005	Not clear, number provided yielded no results	1	15–30
31	1,3,5-Trimethyl benzene	108-67-8	1	Not given

Note: Hazardous ingredients as listed in Section II of product MSDS by name and CAS number. The 20 high-VOC products evaluated contained 31 unique CAS numbers and, thus, 31 different chemicals. The duplication and overlap of the names of ingredients listed under the Hazardous Ingredients column, such as “aromatic” and “aliphatic,” reflect the imprecision of how the chemicals were named on the MSDSs.

^ASkin notation, significant amounts of chemical can be absorbed through the skin and contribute to systemic toxicity.

design of printing presses up to the use of cleanup chemicals on the shop floor (Table VI).

DISCUSSION

Printer Exposure to Cleanup Products

Printers participating in this project were exposed on a daily basis to products containing a high concentration of hazardous solvents (Table II).^(7,14–20) At all shops, hand cleaning the press placed printers’ breathing zones less than an arm’s

length away from solvent-soaked cloths in the absence of local exhaust ventilation to capture the vapors. All printers also had the potential for skin exposure to toxic chemicals while cleaning the press. For half of the high-VOC products in use, this hazard was significantly compounded by the capacity of one or more chemical constituents to be absorbed through the skin in substantial quantities and contribute to systemic toxicity. Although nitrile gloves were generally reported and/or observed to be available, cleaning without gloves was said to routinely occur at one shop and was observed at another.

TABLE IV. Hazardous Ingredients in Alternative Low-VOC (≤ 100 g/L) Cleanup Products by Product (N=14 products)

	Product and Manufacturer (MSDS Date)	Hazardous Ingredients	(%)	CAS No.
1	SOYGOLD 2500 Rinseable Solvent (2/4/05) AG Environmental Products, LLC, Omaha, NE	None listed	N/A	N/A
2	Metalnox M6521 (8/20/04) Kyzen Corporation, Nashville, TN	None listed	N/A	N/A
3	Mirachem Pressroom Cleaner 2501 (7/3/96) Mirachem Corp., Tempe, AZ	None listed	N/A	N/A
4	Mirachem Experimental Commercial Printing Cleaner NP 2520 (8/31/04) Mirachem Corp., Tempe, AZ	None listed	N/A	N/A
5	Magic Wash 522C (4/1/01) Siebert, Inc., Lyons, IL	Fatty esters	70–90	Various
		Surfactants	15–30	Various
6	7858 Envirowash Auto XP Low VOC Automatic Blanket Wash (8/9/02) Anchor Lithkemko, Orange Park, FL	Fatty acid ester	80–100	67762-38-3
		1-Hexadecene	3–7	629-73-2
7	SOYGOLD 2000 (5/1/01) AG Environmental Products, LLC, Lenexa, KS	Alkyl C ₁₆ -C ₁₈ methyl esters	97–99	67784-80-9
		Surfactant	1–3	9016-45-9
8	Magic UV Wash (11/01/01) Siebert, Inc., Lyons, IL	Surfactants	70–90	Various
9	Acetone (4/1/01) Mallinckrodt Baker, Inc., Phillipsburg, NJ	Acetone	100	67-64-1
10	Rho-Solv 7248 (10/21/04) Rho-Chem Corp., Inglewood, CA	Acetone	70–90	67-64-1
		Naptha (light aliphatic)	<10	64742-89-8
		Naptha (light aromatic)	<10	64742-95-6
11	Van Water and Roger Isopropyl Alcohol	Isopropyl alcohol	100	67-63-0
12	Hydro Clean Water Activated Press Cleaner (8/1/98) Lee Chemical Co., Los Angeles, CA	Mineral spirits	Not given	64742-47-8
		Hydrotreated distillate, light	Not given	8052-41-3
		Aromatic hydrocarbon	Not given	64742-95-6
		Xylene	Not given	1330-20-7
		1,3,5-Trimethyl benzene	Not given	108-67-8
		1,2,4-Trimethyl benzene	Not given	95-63-6
		Isopropylbenzene ^A	Not given	98-82-8
13	Glycol Ether DPM (10/05/89) Benco Sales Inc., Crossville, TN	Dipropylene glycol monomethyl ether ^A	> 95	34590-94-8
14	Super Clean T (4/4/00) Super Chem Corp., Anaheim, CA	D-Limonene	<18	5989-27-5
		Propylene glycol n-propyl ether	<25	1569-01-3
		Ethoxylated nonylphenol	<5	9004-87-9

Note: Hazardous ingredients as listed in Section II of product MSDS.

^ASkin notation, significant amounts of chemical can be absorbed through the skin and contribute to systemic toxicity.

TABLE V. Hazardous Ingredients in Alternative Low-VOC Cleanup Products by Chemical (N=20 chemicals)

	Hazardous Ingredients	Chemical Abstract Number (CAS #)	Number of Products with CAS	Concentration % (w/w)
1	None listed	N/A	4	N/A
2	Mineral spirits	64742-47-8	2	Not given to < 10
3	Aromatic hydrocarbon	64742-95-6	2	Not given to < 10
4	Acetone	67-64-1	2	70–100
5	Surfactants	Various	2	15–90
6	Propylene glycol n-propyl ether	001569-01-3	1	<25
7	1,3,5-Trimethyl benzene	108-67-8	1	Not given
8	1,2,4-Trimethyl benzene	95-63-6	1	Not given
9	Xylene	1330-20-7	1	Not given
10	Dipropylene glycol monomethyl ether ^A	34590-94-8	1	> 95
11	D-Limonene	5989-27-5	1	<18
12	1-Hexadecene	629-73-2	1	3–7
13	Isopropyl alcohol	67-63-0	1	100
14	Fatty acid ester	67762-38-3	1	80–100
15	Alkyl C ₁₆ -C ₁₈ methyl esters	67784-80-9	1	97–99
16	Hydrotreated distillate, light	8052-41-3	1	Not given
17	Ethoxylated nonylphenol	9004-87-9	1	<5
18	Surfactant	9016-45-9	1	1–3
19	Isopropylbenzene ^A	98-82-8	1	Not given
20	Fatty acid esters	Various	1	70–90

Note: Hazardous ingredients as listed in Section II of product MSDS.

^ASkin notation, significant amounts of chemical can be absorbed through the skin and contribute to systemic toxicity.

Health Impacts of Alternatives

Printer inhalation exposure to hazardous substances and the environmental emissions that contribute to ozone production should be reduced or eliminated by the use of low-VOC cleanup products. However, printer dermal exposure to cleanup products is not eliminated, and could be exacerbated, by the use of low-VOC alternatives if printers do not use proper gloves. Solvents that do not evaporate quickly may also be more readily absorbed through skin, may stay on the skin for prolonged periods, and may be absorbed in substantial amounts.^(21–23) The use of methyl ester-based low-VOC solvents also carries potential safety (i.e., slipping) and ergonomic implications (i.e., when too much chemical is applied it may take more physical effort to wipe off the low-VOC solvent).⁽²⁴⁾

The alternative cleanup products identified were less hazardous to human health and the environment than high-VOC products in use, as well as being efficacious and cost competitive. However, with the exception of low-VOC content, the occupational and environmental health impacts of the alternatives assessed were not uniform. The range of alternative formulations reflected the trade-offs inherent in developing products for cleaning ink under a variety of circumstances. The toxicity of the low-VOC products ranged from: formulations with no hazardous ingredients listed on the MSDS to products formulated from methyl esters (which clean most types of inks very effectively, have much lower human toxicity than

the organic solvents, and are regarded as environmentally safe)^(13,25,26) to less toxic solvents (acetone or isopropyl alcohol) up to reduced concentrations of highly toxic solvents (Table IV).

Some constituents of the low-VOC products also increased their overall toxicity. For example, one product (Table IV, #6) contained 3 to 7% 1-hexadecene, which has been associated with irritant and allergic skin reactions;^(27,28) another (Table IV, #7) contained 1 to 3% of a surfactant that is an endocrine disruptor (CAS #9016-45-9), the use of which has been restricted in other countries.^(29–31) Another alternative (Table IV, #14) contained less than 5% of an alkylphenol ethoxylate; the exact identity of the chemical could not be abstracted from the MSDS because the CAS number and chemical name were not in agreement. In general, alkylphenol ethoxylates are widely used surfactants that can be microbially degraded in wastewater treatment plants and the environment, leading to the formation of toxic metabolites that exhibit estrogenic activity.⁽³²⁾ The use of lithographic cleanup products with surfactants or other chemicals with endocrine disrupting potential would shift the environmental hazard from air to water.

Other hazardous characteristics of some of the solvent-based alternatives included the use of chemicals: designated with skin notations, i.e., dipropylene glycol monomethyl ether (CAS #34590-94-8) and isopropylbenzene (CAS #98-82-8); causing skin irritation and allergic contact dermatitis, i.e.,

TABLE VI. Opportunities and Barriers to Implementing Safer Lithographic Cleanup Products

Opportunities	Barriers
1 Regulations to improve air quality led to the identification of cleanup solvents that were less hazardous for the environment and workers. The alternative cleanup solvents were competitive in cost and efficacy compared with more hazardous cleanup products. Although worker health and safety did not drive the search for alternatives, occupational health was considered at the beginning of efforts to develop low-VOC alternatives.	Regulations to improve air quality were opposed by some members of the printing industry and have required a significant amount of time to implement; regulations were specific to SCAQMD; they were not implemented statewide; exclusive focus on VOC limits could have led to the development of products with toxic ingredients and unintended health risks to workers and communities.
2 Workers were concerned and interested in their health and safety.	Workers lacked information about the health hazards of cleanup solvents they used even though most had received health and safety training. Workers did not know that less toxic alternatives were available.
3 Representatives of two unions were supportive of worker health and safety and recognized that unionized printers could utilize collective bargaining and grievance processes to encourage the implementation of safer alternatives.	Unions were hard pressed to address the economic and job losses of their members and occupational health was difficult to prioritize in this climate.
4 Some employers had a demonstrated commitment to “greening” their business and had prior experience and success with making changes to comply with environmental regulations.	Production shops lacked the technical expertise to evaluate the occupational and environmental health impacts of alternatives; testing alternatives competed with fast-paced production schedules; some individuals in supervisory positions were resistant to change.
5 Vendors established ongoing relations with press shops and served as a source of information and assistance in purchasing cleanup chemicals.	Chemical companies and suppliers of lithographic cleanup chemicals were generally not engaged in the identification and distribution of safer alternatives prior to the regulation; factors unrelated to occupational and environmental health, cost, or efficacy such as perks and personal relationships, influenced printer cleanup solvent purchasing choices.
6 Manufacturers had factored occupational safety into printing press design, i.e., mechanisms existed to prevent workers’ hands and arms from being caught in machinery.	The design of all printing presses required some worker handling of cleanup solvents. Printing press manufacturers were not in the loop regarding decisions about safer cleanup solvents. A large manufacturer of printing presses could not respond to questions about the compatibility of alternative cleanup products with presses’ seals, information that is relevant to the selection and proper use of cleanup solvents.
7 Representatives of local, state, and federal government agencies supported the linkage of occupational and environmental health and recognized how such linkage could support their agencies’ environmental health-oriented mandates.	With the exception of specific pollution prevention grants which funded collaborative efforts to protect workers, communities, and the environment, there was a shortage of ongoing, institutional, inter-disciplinary mechanisms to leverage the benefits of linking occupational and environmental health.

d-limonene (CAS #5989-27-5),^(14–16) or causing neurotoxicity and skin and respiratory tract irritation, i.e., propylene glycol n-propyl ether (CAS #1569-01-3).⁽³³⁾

Opportunities and Barriers to Implementing Safer Alternatives

Many factors influenced the availability of and printers’ decisions regarding the choice of cleanup products (Table VI).

Regulations

The foremost opportunity was the SCAQMD regulation of VOC emissions from lithographic cleanup solvents. Less hazardous, low-VOC products that were competitive in cost and efficacy compared with high-VOC solvents existed as a direct result of the SCAQMD regulation and related government support for alternatives research and development.

Printers, Unions, Employers

There was interest in implementing safer alternatives among printers and their union representatives, who were concerned about the health impacts of solvent exposure, and employers who had an *a priori* commitment to a "Green Business" model. However, the in-depth evaluation required to investigate and compare the health hazards of new cleanup products was reported to exceed the time or technical expertise of printers in small shops; the vast majority of lithographic printing facilities are small facilities with fewer than 20 employees.⁽³⁴⁾ A program of education, outreach, and technical support would be expected to give printers and employers the tools they need to overcome these barriers.

Supply Chain

A more formidable barrier to implementing safer cleanup products was that printing press and high-VOC cleanup product manufacturers and vendors, who play a central role in printer decision making, did not promote or provide information about alternatives. As a result, printers had to be sufficiently motivated to go outside their established supply chain relationships to seek less hazardous products. The effort and the nature of established relationships with vendors, including friendships and perks, appeared to be strong disincentives to implementing alternatives.

Chemical Hazard Information

This small case study is illustrative of the systemic shortcomings of MSDSs⁽³⁵⁾ and the lack of sufficient publicly available information about the toxicological properties of the vast majority of chemicals in commercial circulation. MSDSs for 7 of 34 (20.5%) total cleanup products assessed in this project lacked essential information such as CAS numbers or concentration data for one or more chemical constituents. Notably, given the potential for printer dermal exposure, the toxicity from skin contact of the very promising solvent alternative, fatty acid esters has not been fully characterized.⁽³⁶⁾

Linkages Between Occupational and Environmental Health

Because occupational health considerations were incorporated at the start of the research and development on alternatives, chemicals that could have met the environmental criterion (i.e., solvents such as methylene chloride that are VOC exempt) but would have introduced serious worker hazards were eliminated from consideration as substitutes. Leveraging environmental regulations to benefit workers also circumvented some of the inadequacies of the current occupational health regulatory apparatus. Current occupational health regulations do not adequately protect printers from their solvent exposure. For example, printer respiratory and neurological symptoms have been documented at air levels far below legal limits,⁽⁵⁾ and regulations permit printers exposed to methylene chloride to incur a risk of 3.6 cancers for every 1000 exposed workers.⁽³⁷⁾

However, reaping the public health benefits of health-protective alternatives to populations outside the reach of a regulation remains a significant challenge. A large study of pollution prevention activities in the hospital industry concluded that legal standards remain important incentives for hospitals to reduce or eliminate hazards.⁽³⁸⁾ A crucial strategy for implementing safer lithographic cleanup products will be to bring regulations in other air districts up to the standards of the SCAQMD. The opportunity to address these challenges exists. Strong, ongoing support for fostering the linkages between environmental and occupational health was found among representatives of local, state, and federal governmental agencies with environmental health-related mandates and who shared a vision and in-depth knowledge of the pollution-prevention approach.

LIMITATIONS

These findings stem from a small convenience sample of printers and shops, and therefore, the degree to which they are representative of the use of cleanup solvents in other lithographic print shops is not known. The descriptive findings regarding the lithographic cleanup work process are consistent with other published reports. The high-VOC cleanup solvents identified in this investigation have been documented in use industrywide.^(1,39) Data from three print shops in this investigation estimated the duration of a printer's use of cleanup solvents to be in the range of 30 to 120 min per day; other reports are in the range of 90 min a day,⁽²²⁾ and between 48 and 180 min per 12-hour shift.⁽⁷⁾ The observation of poor ventilation in small shops and less than universal use of gloves identified in this project have been reported in studies of other lithographic print shops.^(39,40)

The findings regarding the support for change among the employers and printers reflected in this investigation is unlikely to be representative of the industry overall. Participation was subject to strong selection bias for union printers and Green Business employers with an *a priori* interest in health. In general, California printers may also be more aware of environmental issues compared with printers in other locales due to California's more stringent environmental regulations.

We did not collect air monitoring data to document decreases in hazardous printer inhalation exposure. However, the water-based and soy products are very low vapor pressure cleaners. The airborne concentrations of these mixtures would be substantially lower than the airborne concentrations of the currently used cleaners. When acetone is used, it is generally combined with a lower vapor pressure material that reduces its high volatility. Even if the airborne concentrations of the acetone formulations are higher than the concentrations of the currently used cleaners, acetone is lower in toxicity than nearly all other organic solvents.

The backdrop to this project is the transformation of the domestic newspaper and other segments of the lithographic printing industry; these factors were not explored by this project and may be relevant to the implementation of safer

alternatives. The data exclude a key union that, while expressing support for the project's concept, was unable to participate because of its competing priority to address industrywide changes having a direct impact on job losses.

Finally, a significant limitation of this project is the lack of follow-up to evaluate how the alternatives fared over time. Good industrial hygiene practice dictates that employers evaluate the impacts of changes to the work process on employee exposures and ensure that new safety hazards were not introduced into the work environment by these changes. Such timely follow-up also represents an important area for further research.

CONCLUSIONS

Employers should implement low-VOC, low-toxicity cleanup products in a timely manner to protect the health of printers and the environment. Low-toxicity, not just low-VOC content, are critical criteria for choosing alternative cleanup products, but the lack of information about the toxicity of chemicals was an impediment to evaluating alternatives. Employers should not purchase cleanup products that do not have a complete MSDS and should avoid products formulated with chemicals that: (1) are designated with skin notations; (2) cause respiratory irritation or other acute health effects at low levels of exposure; (3) are linked to chronic health impacts such as cancer, reproductive and developmental effects, irritant and allergic skin reactions, and neurotoxicity; and/or (4) are endocrine disruptors.

Use of low-VOC lithographic cleanup products does not mitigate the potential for printer dermal exposure and may carry safety and ergonomic implications. Employers should: (1) seek evidence from glove manufacturers to demonstrate the efficacy of nitrile or other barriers when used with alternative lithographic cleaning products; (2) maintain vigilant housekeeping to prevent a slipping hazard; (3) retrain workers on appropriate and safe use of alternatives; and (4) evaluate the impacts of changes to the work process on employee exposure in a timely manner. Lithographic cleanup solvent manufacturers should seek low-VOC ingredients that do not pose a dermal exposure hazard.

Linking environmental and occupational health at the initiation of research and development of alternative lithographic cleanup solvents prevented the development of substitutes that would have introduced worker hazards, and provided an opportunity to circumvent some of the inadequacies of the current occupational health regulatory apparatus. Governmental organizations should establish and maintain institutional interdisciplinary mechanisms to support these linkages.

ACKNOWLEDGMENTS

We are indebted to the printers, their union representatives, and to the employers who generously shared their abundant knowledge and scarce time. Without their participation, this project would not have been possible. This

project was conceived of, and funded by, the California Department of Public Health, Hazard Evaluation System and Information Service, and conducted by the University of California, Berkeley, School of Public Health through a contract with the Public Health Institute (Contract #02694-01-01).

Financial support, and/or in-kind collaboration for the workshop and demonstration project came from the U.S. Environmental Protection Agency, Region 9, the California Department of Toxic Substances Control, the Bay Area Air Quality Management District, the City and County of San Francisco, Department of Public Health and Department of the Environment, the Alameda County Green Business Program, and the Northern California Media Workers Union, Local 39521, Communications Workers of America. The participation of all of these collaborators was essential to this effort.

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